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W. R. Morgan and A. H. Charles

The Development of a Reflector Enamel

THE DEVELOPMENT OF A REFLECTOR ENAMEL

BY

WILLIAM RAY MORGAN
AND
ANDREW HOYLE CHARLES, JR.

THESIS

FOR THE

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DEGREE OF Bachelor of Science

Cullen W. Parmelee

Instructor in Charge

APPROVED: C. W. Parmelee

HEAD OF DEPARTMENT OF Ceramic Engineering

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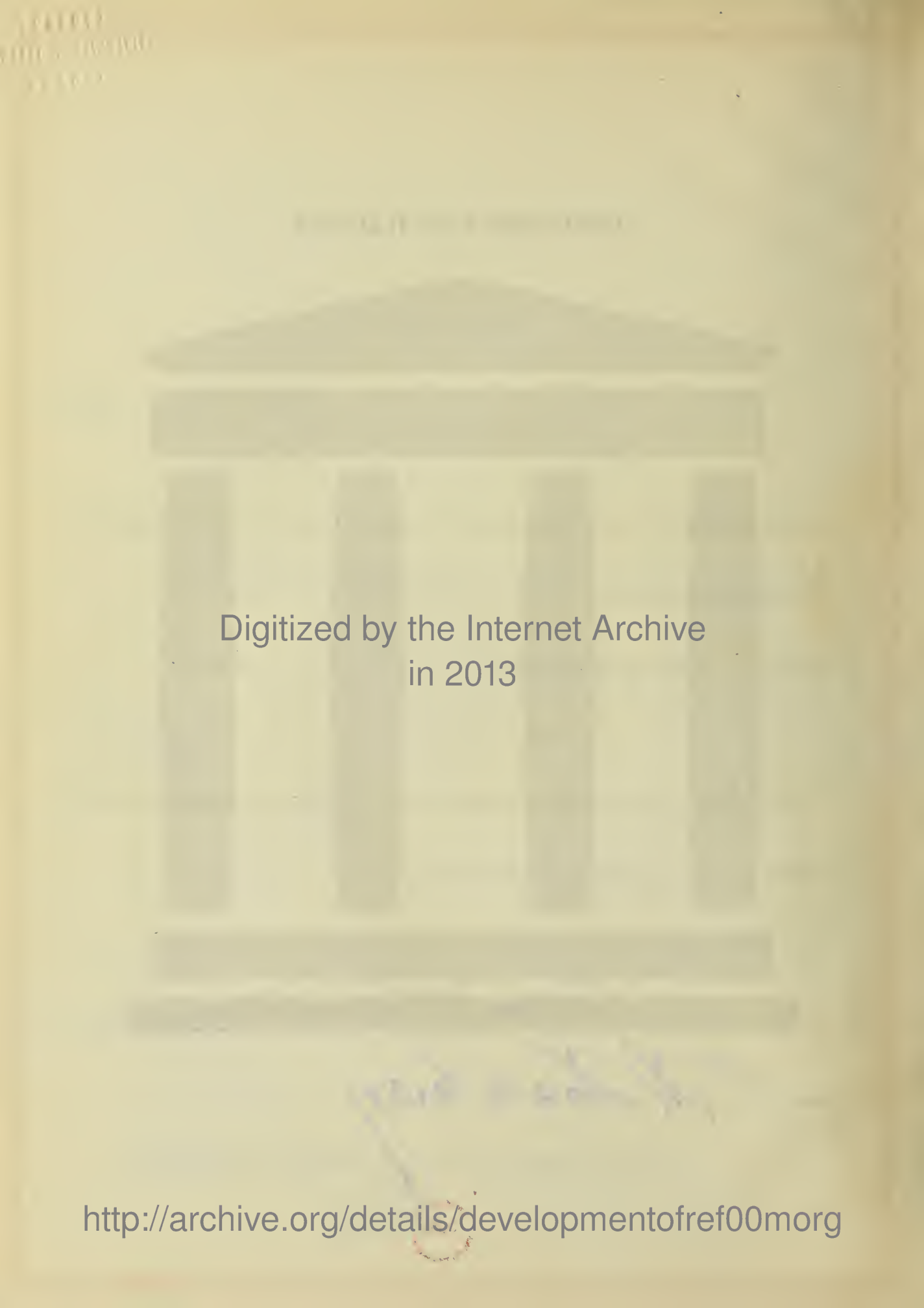
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THE DEVELOPMENT OF A REFLECTOR ENAMEL.

I INTRODUCTION

The application of enamel to steel to produce a reflecting surface for light is a comparatively recent development, and each year shows an increase in the manufacture of such products.

An enamel suitable for reflector purposes must have a coefficient of expansion such that it will adhere to the metal, be able to withstand sudden impacts, possess and retain a high reflective power, and have such a surface that it can be easily and effectively cleaned. The increasing popularity of enameled reflectors over other types is due in the main to their unbreakableness.

The ability of enamels to reflect light is due to their opacity, which is produced by various opacifying agents. Opacifiers are characterized by higher indices of refraction than the enamel glass in which they are suspended. The theory is that the light striking the particles with indices of refraction greater than that of the glass, in which they are embedded, is deflected in various directions. Since with finely divided opacifiers there are multitudes of these particles in each small section of the enamel, and they are embedded in the glass at all sorts of angles, the diffusion of light is so great that the enamel becomes opaque white.

Opacifying agents in enamels are divided according to their effectiveness into (1) true opacifiers, and (2) accessory opacifiers.[1] True opacifiers include the oxides or other compounds of tin, antimony, arsenic, zirconium, titanium and calcined spinels. The most important accessory opacifiers are fluorspar, cryolite, bone-ash, and silica. Since true opacifiers are chemically inert they merely form suspensions in the fused enamels. The high and increasing cost of tin oxide, the commonly used opacifier, led the writers to investigate

1. H.F. Staley. Technologic Paper 142, Bureau of Standards.

the possibilities for an economical substitute. Limited time has confined the investigation to zirconia and spinel, which in the minds of the writers offer the best promise. The relative cost of the three opacifiers in barrel lots is as follows:- tin oxide 65, zirconia 40, spinel 35 (estimated).

Preliminary work on the ground coat was necessary in order to obtain a suitable composition upon which to apply the cover coat. The use of nickel and cobalt oxide in ground coats for sheet steel has been a matter of lengthy and varied discussion for a long time. The authors' intentions were to determine the effect of these oxides and the percentages of each necessary to produce the best enamel.

II PURPOSE

1. To determine the combined effect of cobalt and nickel on ground coats for sheet steel enamels.

2. To investigate the possibilities of substituting a less expensive opacifier for tin oxide in reflector enamels.

III EFFECT OF COBALT AND NICKEL OXIDES ON GROUND COATS

A. Previous Investigations

The importance of cobalt and nickel oxides in ground coats affords a fertile field for discussion. Although much work has been done on the subject, there is still some question as to the value of cobalt oxide in a ground coat enamel.

Dr. Grunwald says, "Cobalt oxide possesses valuable physical characteristics, which make it suitable for the preparation of ground coat enamels."[2] He derives his conclusion from the fact that the

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2. Enameling on Iron and Steel. Grunwald, p 22.

coefficient of expansion is as nearly as possible the same as that of sheet iron. This, however, is disputed by Moyer and Havas[3] who find that ground coat enamels have a much lower coefficient of expansion than sheet steel.

The most generally accepted theory of the function of cobalt in ground coat enamels was first advanced by Dr. Vondracek[4] who said that the iron, at the melting temperature of the ground coat, is oxidized at the expense of cobalt oxide and that the latter or rather the cobalt silicate is changed to a compound of lower oxygen content or the cobalt oxide is even reduced to the metal. As a result, the clean surface of the steel is attacked so that the enamel joins very intimately with the metal and the danger of chipping off of the coats is lessened.

C. Fostman[5] in his discussion of the function of cobalt oxide says:- "Only in cobalt oxide ground coats does a blue color appear on smelting. If one should discontinue the heating just at this point, it would not adhere firmly enough to the steel, even though it had already become molten and glasslike. Also, one can burn it so long that the color becomes black. Now how is this color change, which is so markedly essential for a proper adhesion to be explained? The only explanation I find for it is that the enamel has taken up the iron from the surface in some form of oxidation." He further states that while oxygen might come from the air in the muffle, it is more probable that it is given up by the cobalt oxide, which is reduced to metallic cobalt. He also considers the cobalt an indicator for

---

3. Chem. Ztg. Vol. XXXIII, p 1314.
4. Sprechsaal 1909, No.14.
5. Keramische Rundschau XIX, pp 5, 65, and 107.

correct burning of the enamels. These small amounts of very finely divided metallic cobalt could then perhaps form a very porous alloy with the iron on the surface of the shape. To this the enamel would be able to adhere firmly, which the silicate flux would take the place of the cobalt, while alloyed with the iron." He gives as an argument that this oxygen is furnished to the iron by the cobalt and not from any other source, the fact that in ground coats, which are not colored by cobalt "an exceedingly smaller change in color takes place during burning."

Dr. Bela Havas[6] agrees with Tostman on the reduction of cobalt silicate, indicated by a change of color from a blue to a green, but states that it is improbable that the reduction of cobalt silicate at the temperature involved would go far enough to produce metallic cobalt.

Mayer and Havas[7] have shown that iron reduces tin oxide to tin; hence cover coats applied directly on iron result in dark enamels. Reduction of PbO to Pb was also noted. Vondracek[8], however, refutes the statements of Mayer and Havas in regard to reduction of SnO_2, but states that the ground enamel is necessary to prevent oxidation of the carbon in the iron as well as of that of the latter.

Coe[9] gives the following properties as essential to a good ground coat:- (1) Begins to fuse at a dull red heat and retains a good gloss throughout a wide heat range. (2) Dissolve any foreign matter on the surface of the metal. (3) Low viscosity. (4) Not contain or absorb any injurious gases such as SO_3. In a summary of his results

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6. Sprechsaal XLIV, 72-3.
7. Sprechsaal XLIII, 729-9.
8. Sprechsaal XLIV, 115.
9. T.A.C.S. Vol.13, 531-549.

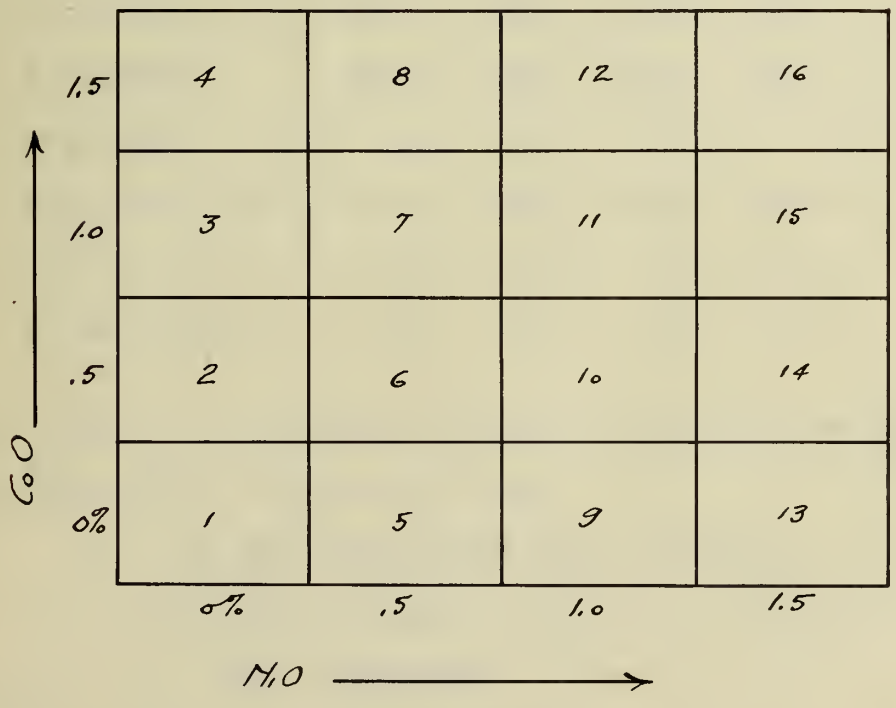
he states that Co_3O_4 is of little or no value in ground coats.

The noticeable feature in much of the previous work done by others is the fact that the investigators as a rule are prone to make sweeping statements, as to the worth of cobalt and nickel oxide, without subjecting the trials to adequate tests. In numerous cases the authors go so far as to make assertions without describing any tests whatsoever.

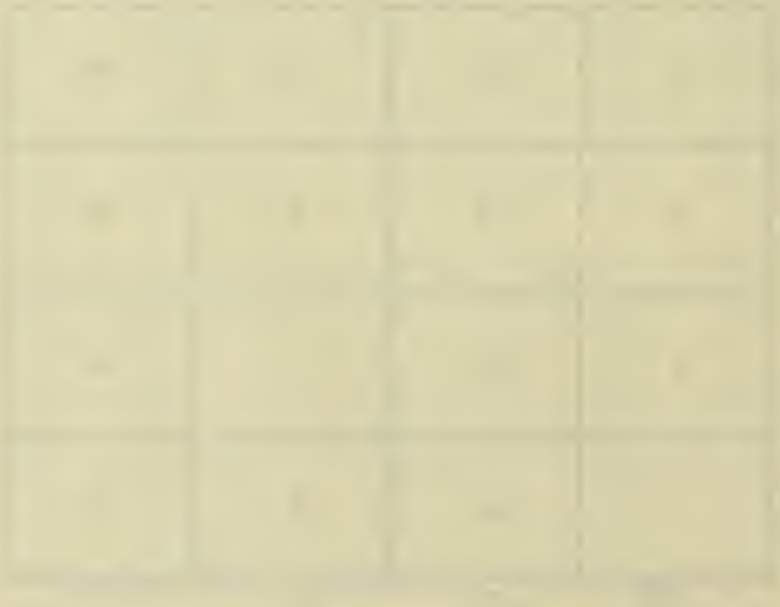
B. Execution of Work

1. Field Covered. A series of ground coat formulas in commercial usage was consulted and the most representative of the group was selected as a basis for the field.

FIELD OF GROUND COATS



The average cobalt content in the formulas consulted was approximately .65%, while nickel was somewhat less. The above limits are



considerably higher than the average, but the writers were desirous of investigating the effect of additional increments of both color oxides.

The members were numbered as indicated in the above diagram of the field. The batch weights and ceramic formulas of the corners are as follows:

BATCH WEIGHTS

Frit

	A	B	C	D
Borax	101.0	101.0	101.0	101.0
Feldspar*	101.0	101.0	101.0	101.0
Quartz	73.5	73.5	73.5	73.5
Soda Ash	25.0	25.0	25.0	25.0
Saltpeter	23.0	23.0	23.0	23.0
Fluorspar	26.0	26.0	26.0	26.0
Magnesia	1.0	1.0	1.0	1.0
Manganese Oxide	12.0	12.0	12.0	12.0
Cobalt Oxide	5.4	5.4	0.0	0.0
Nickel Oxide	0.0	5.4	0.0	5.4

To 1000 gms. of the above frits the following amounts of raw materials were added in the mill mix

90 gms. Tennessee Ball Clay No.7

1.5 gms. Borax

1 gm. Magnesia

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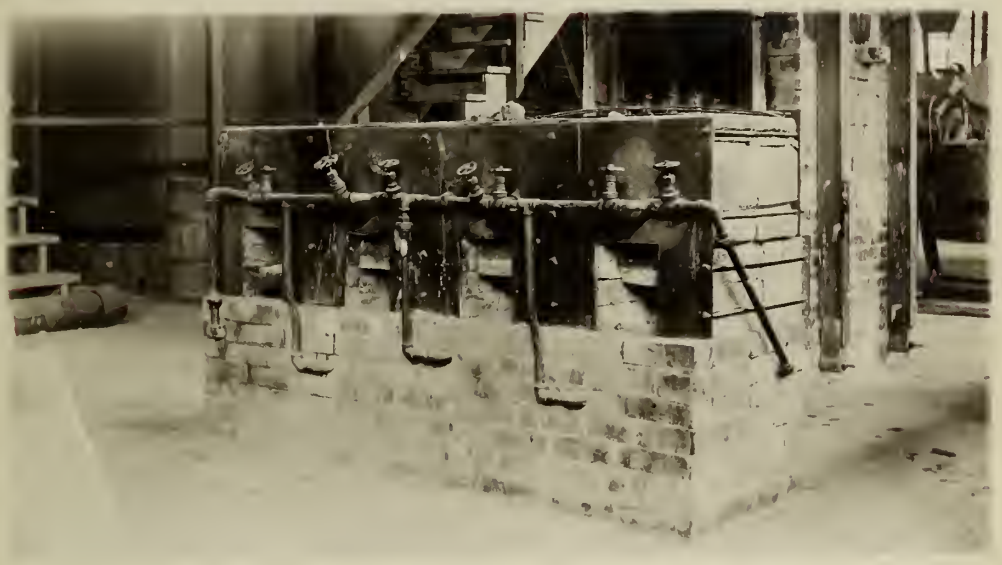
*Analysis of Feldspar

Na_2O	3.7per cent	SiO_2	70.2 per cent
K_2O	7.8	CaO	.9
Fe_2O_3	0.2	MgO	trace
		Al_2O_3	16.3 per cent

Ceramic Formulas of Frits

A	.295 Na_2O		
	.246 K_2O		
	.279 CaO	.151 Al_2O_3	1.930 SiO_2
	.010 MgO	.442 B_2O_3	.279 F_2
	.115 MnO		
	.055 CoO		
B	.279 Na_2O		
	.234 K_2O		
	.265 CaO		
	.009 MgO	.143 Al_2O_3	1.830 SiO_2
	.109 MnO	.418 B_2O_3	.265 F_2
	.052 CoO		
	.052 NiO		
C	.310 Na_2O		
	.262 K_2O		
	.295 CaO	.160 Al_2O_3	2.480 SiO_2
	.011 MgO	.468 B_2O_3	.295 F_2
	.122 MnO		
D	.294 Na_2O		
	.246 K_2O		
	.278 CaO	.151 Al_2O_3	1.930 SiO_2
	.010 MgO	.442 B_2O_3	.278 F_2
	.115 MnO		
	.055 NiO		

2. Preparation of Enamels. The four corners of the field were weighed out and thoroughly mixed by passing several times through a 20-mesh screen. The members were fritted in fireclay crucibles (1 1/2 kg. capacity raw materials) in a gas-fired frit furnace.



Fritt Furnace

The orifice of the crucible was daubed with wadding until the melt was homogeneous and free from bubbles as determined by inserting a clean steel rod. When the melt was of the proper consistency, it could be drawn out into a thin, clear thread. After this state has been reached the wadding was removed and the fritt was allowed to drop into water, which was agitated so as to render the fritt more friable, thus facilitating grinding.

The fritt was ground wet in porcelain mills so as to pass a 200-mesh sieve . The ground fritt was dried, and the mill mix as given above was weighed and added to the proper amount of water and ground

Ball Mill Racks

in a porcelain mill for one hour to insure a thorough mixing. The enamel was passed through a 150-mesh screen. The intermediate members were obtained by blending the four corners. The water factor, i.e., ratio of weight of given amount of slip to its content of dry enamel, which gave the most satisfactory results, was 1.5 .

3. Preparation of Trials. It is generally conceded that cleanliness of the steel is imperative in successful enameling. Cleaning as applied to steel embraces both scaling and pickling. [illegible]-complished by placing the ware in a muffle kiln, similar to an enamel oven at 1200°F. for about 5 minutes. To assist in the formation of a light scale, which will easily separate from the metal, the ware may be sprinkled with dilute acid, usually discarded acid from the pickling tanks.[10] For rusted ware this procedure is especially

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10. Cleaning Sheet Iron and Steel. Danielson, J.A.C.S., Nov. 1919

advantageous in that it facilitates the subsequent pickling. The purpose of scaling is to remove all dirt and grease inground in the pores of the metal during the machine operations. In view of the fact that the trials were not subjected to machine operation the process of scaling was omitted.

The trials were placed in a 12% solution by weight of commercial muriatic acid for about 20 minutes. Stronger acid should be avoided[11]. The objection being that such tends to blister the steel either during the pickling or the enameling operations. After this treatment the ware was placed in a bath of water, where each trial was sponged. They were then rinsed in a second bath of water after which they were immersed in a weak solution of soda ash. It is essential that all traces of acid be removed and that there be a slightly alkaline reaction on the surface of the ware. Should any acid remain on the ware, it may give rise to dipping irregularities and blistering during burning. If the soda ash solution is too concentrated, crystals of sodium carbonate will be deposited which give rise to a bubble structure during burning and a decided reduction in the heat range. The solution employed contained about 30 grams of soda ash to a gallon of water. This solution was heated to about 80°C. The transfer of ware from the alkaline bath to the dryer should be effected as rapidly as possible so as to prevent rusting.

4. Application and Burning. The ground coats were all applied by hand dipping. The attempt was made to obtain on all of the trial pieces a coating uniformly thick by using enamels of approximately the same water content and allowing all superfluous enamel to drain off.

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11. C. Treischel Jour.Amer.Cer.Soc., 2-744 (1919).

Enamel Oven

After thorough drying in a steam heated dryer the pieces were burned in a small gas fired muffle oven. All heat treatments are a function of time and temperature and since each trial was burned to maturity, it was necessary to investigate only the effect of burning at different temperatures. Having in view the choosing of a temperature which would produce a mature enamel in a reasonable length of time and also develop a good color, a minimum temperature of 900°C., a moderate temperature of 950° C., and a maximum temperature of 1000°C. were chosen.

Six trials of each enamel were burned at each of the three temperatures, very close regulation of temperature being possible. Of the six pieces, one was to be used for exhibition, two for tin cover coat blanks, and the remaining three for the impact test.

5. Tests. Two tests were employed for the determination of the

effect of the variation in content of cobalt and nickel oxides upon a ground coat.

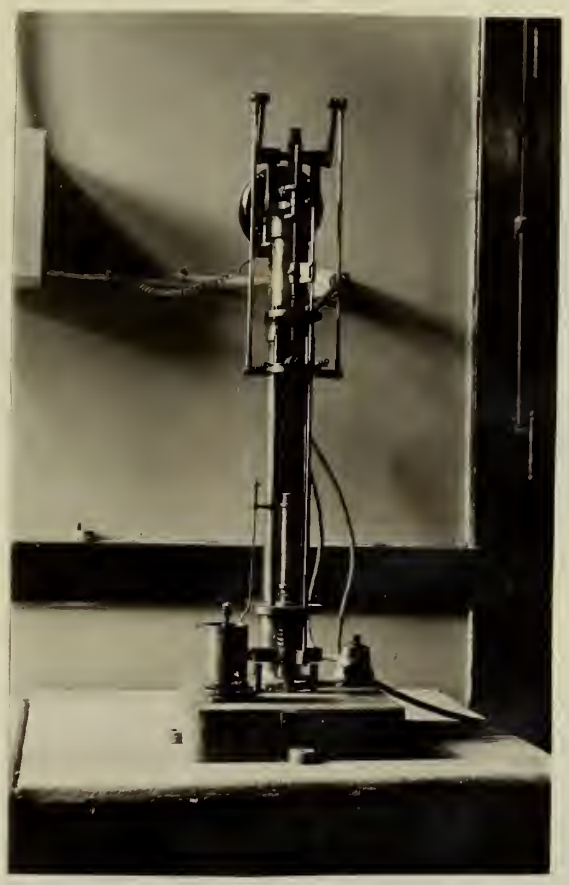
1. Color and texture.

2. Impact test.

No definite standards are in practical use for the determination of color and texture. Hence the physical appearance to the unaided eye was used as a basis of comparison of these properties.

The field of best color and texture was selected to be subjected to the impact test.

The impact tests were made with a standard impact test machine.[12]



Page Impact Machine

The machine was an electrically driven hoist which alternately elevated and tripped a one kilogram weight at a desired height. Failure varied with the number of blows and with the distance the hammer fell

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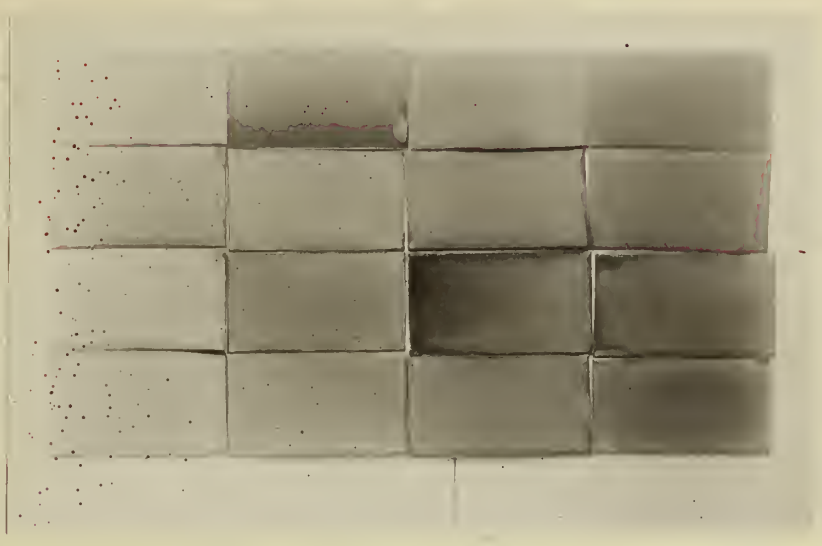
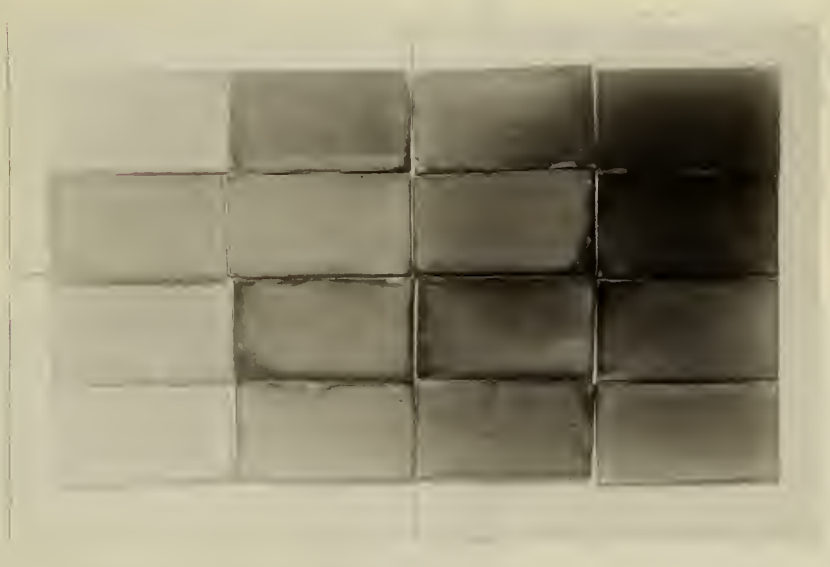
12. F.L. Nichols Co., Washington, D.C.

Ground Coat Fields

900°



950°



1000°

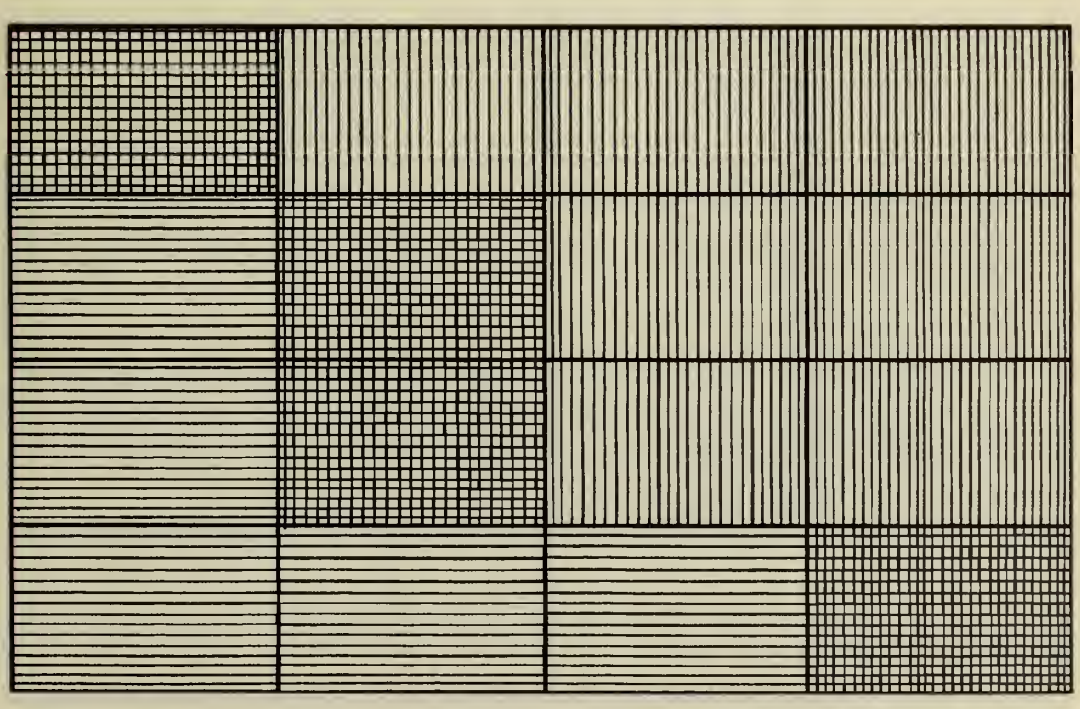
GROUND COAT FIELD BURNED AT 900°C.

% NiO →

% CoO	0.0%	0.5	1.0	1.5
1.5	DEEP COBALT BLUE 4	DEEP BLUE 8.	GREYISH BLUE 12.	DARK BLUISH GRAY 16.
1.0	LIGHT COBALT BLUE 3	BLUE 7	GRAYISH BLUE 11	BLUISH GREY 15
0.5	PALE BLUE 2	DEEP LAVENDER 6	STEEL GREY 10	DARK GREY 14
0.0	MANGANESE PINK 1	LIGHT MANGANESE BROWN 5	LIGHT CHOCALATE BROWN 9	DARK BROWN 13

% NiO →

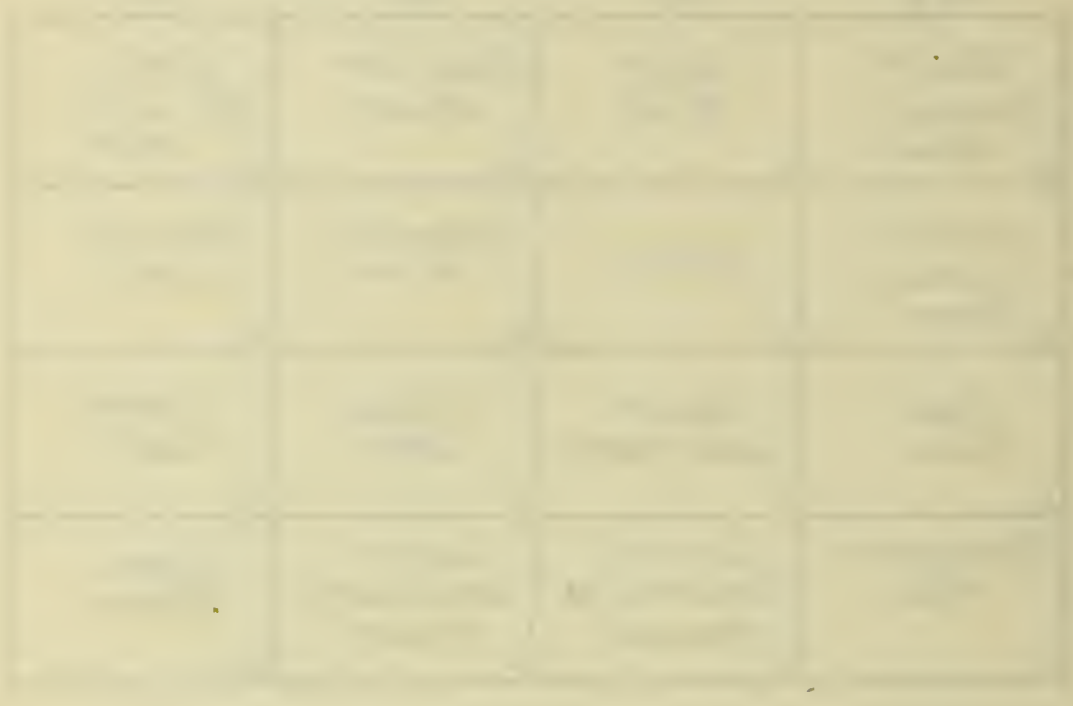
% CoO ↑



SMOOTH, FINE TEXTURE

PINHOLED, COARSE TEXTURE

FINE EGGSHELL TEXTURE



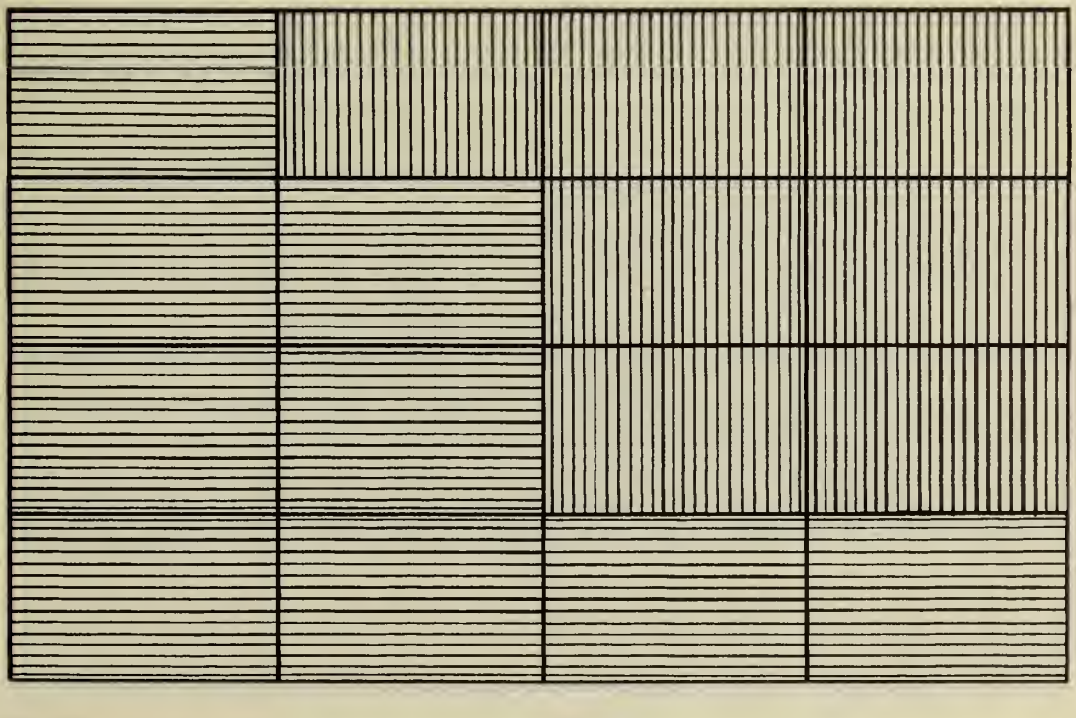
GROUND COAT FIELD BURNED AT 950°C.

%NiO →

%CoO	0.0	0.5	1.0	1.5
1.5	DEEP COBALT BLUE 4.	VERY DEEP BLUE 8.	DARK GREYISH BLUE 12.	DARK BLUISH GREY 16.
1.0	DEEP COBALT 3.	GREYISH BLUE 7.	DARK GREYISH BLUE 11.	DARK BLUISH GREY 15.
0.5	LIGHT BLUE 2.	DEEP LAVENDER 6.	GREY 10.	DARK GREY 14.
0.0	DEEP MANGANESE PINK 1.	LIGHT BROWN 5.	CHOCOLATE BROWN 9.	DARK BROWN 13.

%NiO →

%CoO ↑



FINE EGG-SHELL TEXTURE

FINE SMOOTH TEXTURE

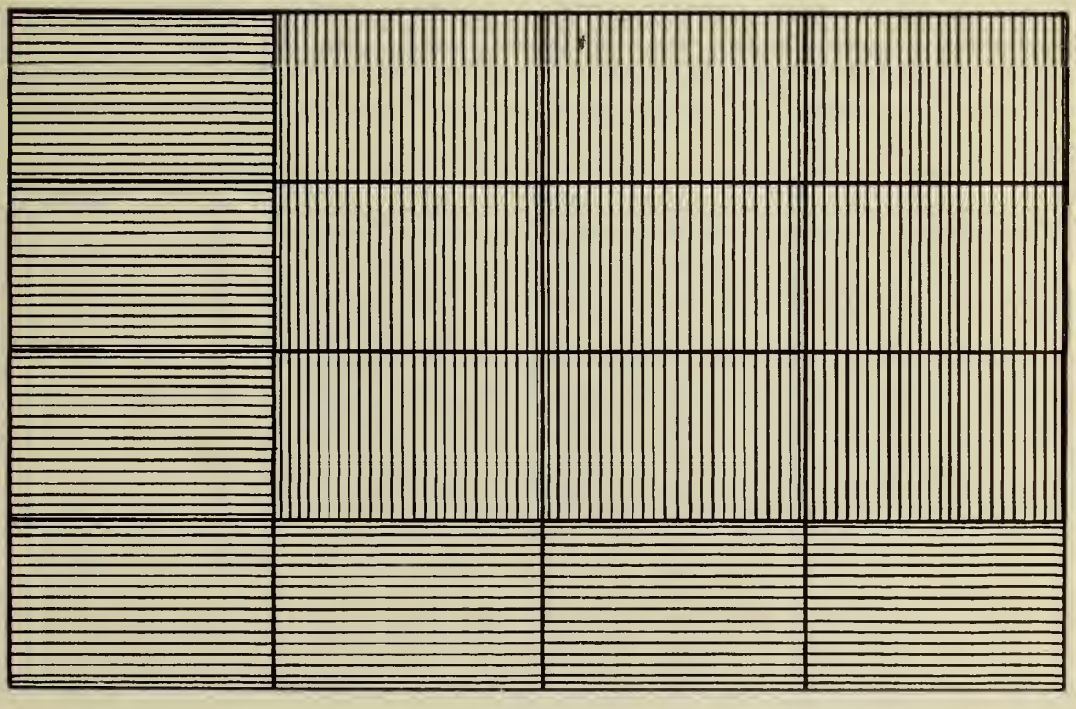
GROUND COAT FIELD BURNED AT 1000°C

% NiO ——————→

% CoO	0.0 %	0.5	1.0	1.5
1.5	DEEP COBALT BLUE 4	BLUE BLACK 8	BLUE BLACK 12	BLUE BLACK 16
1.0	DEEP COBALT BLUE 3	" 7	" 11	" 15
0.5	LIGHT BLUE 2	" 6	" 10	" 14
0.0%	VERY DEEP MANGANESE PINK 1	BROWN 5	DARK CHOCOLATE BROWN 9	DEEP OLIVE BROWN 13

% NiO ——————→

% CoO ↑



SMOOTH TEXTURE, OVER-BURNED AND PARTIALLY HEALED

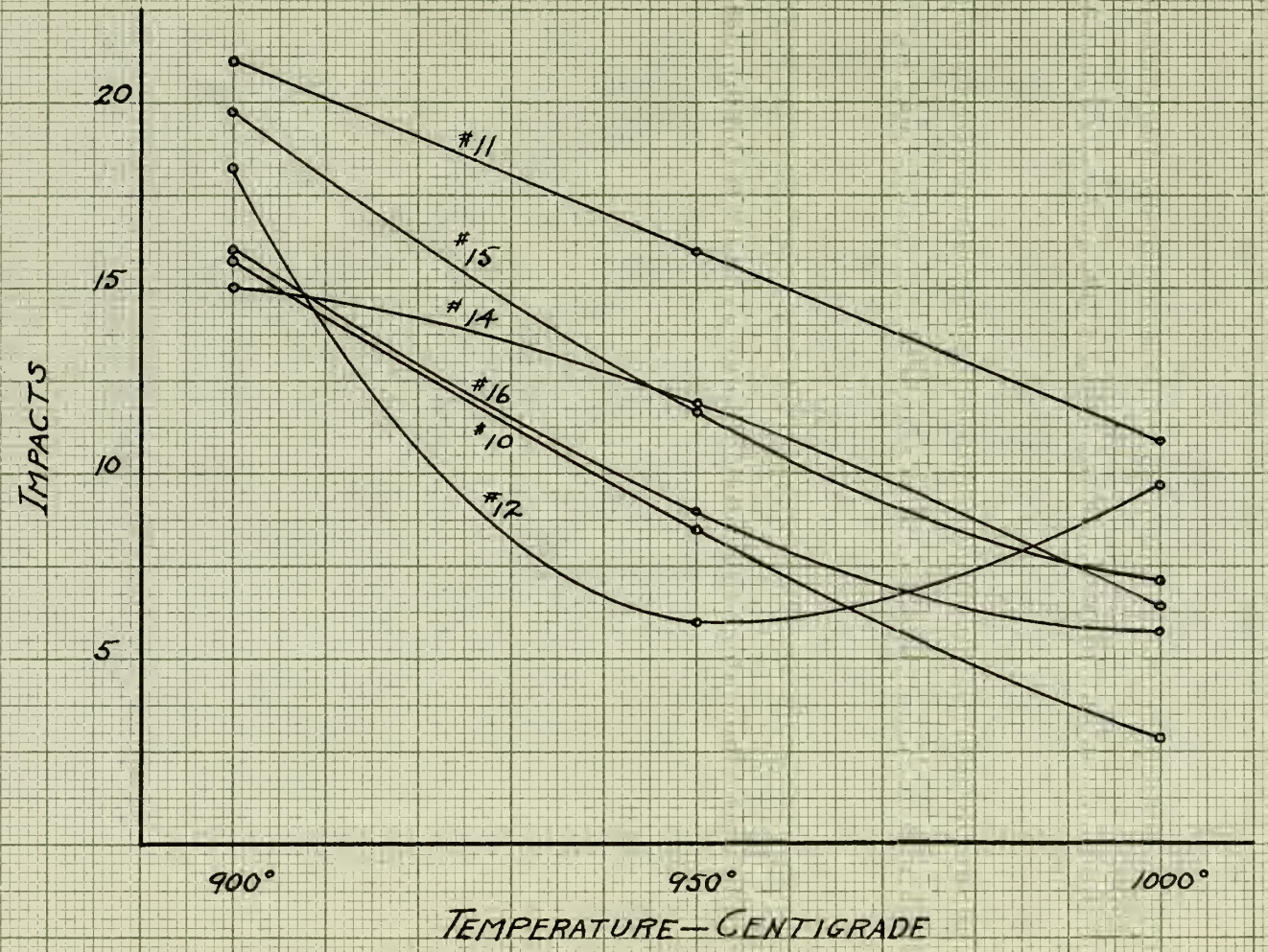
ROUGH TEXTURE DISTINCTLY OVERBURNED

NUMBER OF BLOWS

Temp.	Composition Number					
900°	10	11	12	14	15	16
	15	20	16	10	15	15
	15	22	16	13	15	15
	16	21	15	13	22	14
	16	22	18	12	22	14
	17	22	17	13	20	18
	15	20	22	17	19	17
	17	21	24	20	20	16
		21	18	17	20	17
			18	20	21	17
			19		19	17
Avg.	15.8	21.1	18.3	15.0	19.8	16.0
950°	10	14	7	11	11	10
	8	17	6	12	10	10
	9	16	7	12	10	9
	8	20	6	11	11	9
	9	16	5	11	13	10
	7	14	5	12	13	8
	8.5	16	5	12	10	8
	8	17	7	13	12	8
	7	15	6	12	14	9
	10	14	7	12	14	8
Avg.	8.5	15.9	6.1	11.8	11.7	8.9
1000°	4	10	12	9	4	7
	2	10	12	6	7	8
	2	9	10	5	6	7
	3	10	10	6	8	5
	2	11	8	8	6	6
	3	13	10	7	7	7
	2	14	9	8	7	5
	5	10	8	7	9	5
	2		10	5	8	5
	3		8	5	9	3
Avg.	2.8	10.8	9.7	6.4	7.1	5.8

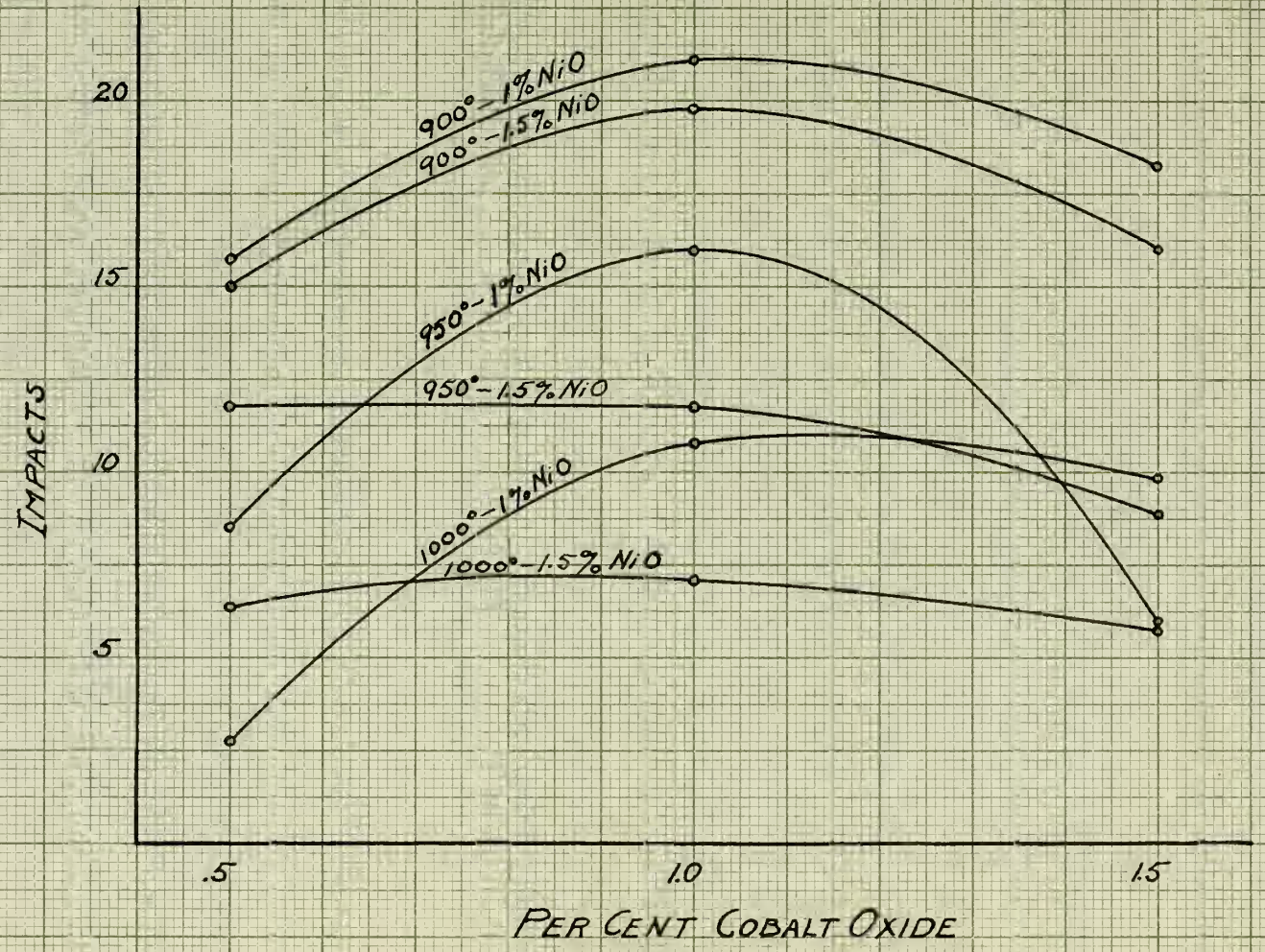
No I

GRAPH SHOWING THE EFFECT OF TEMPERATURE ON TOUGHNESS



No. II

GRAPH SHOWING EFFECT OF VARYING COLOR OXIDES ON TOUGHNESS



The effective height giving the best range in number of blows required to produce failure was 3.2 cm. in our case. The point of contact of the hammer with the enamel was the surface of a 3/4" steel ball, this giving practically a single point contact. The number of blows required to cause failure of the enamel gave a comparison of the relative toughnesses of the respective compositions.

Failure was characterized by a round straight sided hole about 3/32" in diameter through the enamel. The approximate number of blows required to produce failure was determined on the first test of each composition. On the succeeding tests the trial was examined a few blows before failure was reached and the powdered enamel, if any, removed. The trial was then subjected to single blows until examination showed complete failure, any powdered enamel being removed after each blow with the point of a knife as before. The average of ten tests was taken on each enamel composition at each of the three temperatures, four tests being made on each trial piece. The pieces were supported on the flat machined steel base of the machine itself.

D. Summary of Results

I. Effect of temperature upon color and texture.

(a) 900°. Pinholing seems to be prevalent in the line of no cobalt and the line of no nickel. This condition is alleviated both in the region of high cobalt and of high nickel. The trials which are satisfactory as to texture are Nos. 8, 10, 11, 12, 14, 15, 16.

In each line of constant nickel there is an increase in the intensity of color with each additional increment of cobalt oxide. In the lines of constant cobalt and increasing nickel, there is a

gradation from a typical cobalt blue to a bluish gray. There is a distinct segregation of coloring pigment in the area of the field high in cobalt and low in nickel. This defect is remedied with addition of nickel oxide. Likewise in the area of low cobalt and high nickel, the same difficulty is experienced although it is not quite so noticeable as in the case of high cobalt. This defect is corrected in the field of high cobalt. Finally, we find the field of most uniform color distribution that in which we have large amounts of both coloring oxides. Nos. 10, 11, 12, 14, 15, 16, were the only trials which qualified as to color and warranted further consideration.

In the above named field the trials which show the best maturity are those in which the true cobalt color is changing to a greyish blue. Considering both texture and color the only trials qualified for further testing are Nos. 10, 11, 12, 14, 15, 16.

(b) 950°. In the line of low cobalt and the line of low nickel, the pinholing is less noticeable than at 900° but in the field of best enamels as described above, there is slight pinholing. None of the field is as good as the previously selected field.

As before, in each line of constant nickel and each line of constant cobalt there is an increase in the intensity of color with the increase of cobalt and nickel respectively. On the whole colors at 950° are deeper than at 900°. The segregation is more pronounced than at 900° and does not completely disappear even with the highest color oxide content.

In general considering both color and texture, 950° gave less satisfactory results than 900°.

(c) 1000°. The line of low cobalt and line of low nickel shows a rather smoother surface than does the portion of the field

high in color oxides. This fact is probably due to overburning of these members and consequently the gas bubble pits heal over more readily. In the region of increasing cobalt and nickel, the gas bubble structure is characteristic and the surface has a rough texture. In this series, no color segregation is noticeable due to the complex bubble structure. In the field of high color oxides there is no variation in color of the trials for added increments of color oxides.

This temperature does not give satisfactory color or texture and is unquestionably not suitable for bringing out the best qualities of the particular field.

Finally, from the above results, we deduce that 900°C. is the most favorable temperature for developing the best color and texture; and that the area of the field in this range which warrants further consideration consists of Nos. 10, 11, 12, 14, 15, 16.

Compositions showing the best maturity are those in which the true cobalt blue color has just changed to a greyish blue.

II. Impact Test.

(a) Effect of temperature on toughness. All compositions show decreasing toughness with increase of temperature, No. 12 excepted. This digression, however, is attributed to experimental error probably due to lack of uniformity of dipping. At all temperatures No.11 shows the greatest toughness, No.15 being next best.

(b) Effect of varying color oxides on toughness. With constant nickel, beginning at .5% CoO, increasing toughness is developed with increasing CoO until a maximum is reached at 1% CoO, after which further additions of CoO up to 1.5% cause a decrease in toughness.

Greater toughness was developed in the series containing 1% nickel than in the one containing 1.5% at 900°C.

In compositions of 1.5% and .5% CoO at 950°, greater toughness was developed with 1.5% NiO, however with 1% CoO greater toughness was attained with 1% NiO.

In the composition containing .5% CoO at 1000° greater toughness was gained with 1.5% NiO. While with 1% and 1.5% CoO greater toughness was developed with 1% NiO.

In all cases the maximum toughness was attained with 1% CoO. Considering the line of maximum toughness at 1% CoO, the effect of nickel is shown, in that in every instance greater toughness was developed with 1% NiO than with 1.5% NiO.

Maximum toughness in the entire field was developed with the combined effect of 1% CoO and 1% NiO, i.e., No.11. This composition was therefore selected to be used in the subsequent investigation of opacifiers.

E. Conclusions

1. The presence of nickel is conducive to the development of a uniform color.

2. An increase in per cent of total color oxide content decreases pinholing at the proper maturing temperature.

3. Cobalt oxide is valuable as an indicator of maturity.

4. Maximum toughness is developed with 1% CoO and 1% NiO. Further additions of either oxide decrease toughness.

5. Maximum toughness is attained at 900°C.

6. The amount of cobalt oxide necessary to produce a satisfactory ground coat is in excess of that used in general practice.

F. Comparison of Results and Conclusions

Following is a discussion and comparison of the above results with those obtained by several other investigators of the same subject.

In agreement with R.R. Danielson[13], the authors find (1) an increase of both nickel and cobalt oxides decreases pinholing; (2) cobalt enamels show a greater toughness; (3) Combined cobalts and nickel are useful as an indication of the maturing point of the enamel. Danielson, however, did not connect his statements on toughness with amount of color oxide used.

Landrum[14] states that cobalt is a necessary ingredient in ground coats for two reasons:- (1) It is an indicator of the point of correct burning. (2) Cobalt ground coats adhere to the metal more firmly than those not containing the metal. A non-cobalt ground coat may be improved by the addition of proper amounts of cobalt oxide. These results are in accordance with those obtained by the writers, except that Landrum does not define any point of maximum toughness.

Shaw[15] says: "In ground coats the changing of the color from a blue to a black is an excellent indication of proper burning. Good ground coats can be made without the use of cobalt oxide." The writers found from their investigation that only the compositions containing both cobalt and nickel changed color at the point of maturity. The compositions containing cobalt alone remained a deep blue up through the highest temperature of burning (1000°C). The writers agree with Shaw in that cobalt is not absolutely essential, but as demonstrated by the foregoing results definite benefits are

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13. T.A.C.S. Vol.XVIII - 343.
14. T.A.C.S. Vol.XIV - 756.
15. T.A.C.S. Vol.XI - 115.

derived and the quantities and cost of the cobalt oxide used are not such as to prohibit its use.

IV SUBSTITUTION OF OPACIFIERS FOR TIN OXIDE

A. Previous Investigation

Zirconia. Hartman found that "Upon substituting 5-10% SnO_2, in the usual enamels, by the same amounts of ZrO_2, the covering power of the enamel is decreased. More of the latter is therefore required to accomplish the same purpose. Zr borate was found to be an excellent opacifier in which case the B_2O_3 of the enamel must be decreased correspondingly. The use of fritted ZrO_2 increases the acid resisting power of the enamel. The function of the ground coat is supposed to be the protection of the SnO_2 from reduction by Fe. The use of less easily reducible opacifiers might do away with the ground coat. The use of ZrO_2 enamels might have some influence in this direction since it, as well as the borate, is very resistant toward reduction."[16]

Grunwald[17] doubts the efficiency of Zirconia as an opacifier and attributes the satisfactory results obtained by Hartman to the high content of ZrO_2 (14%) and of cryolite (21%).

"The use of pure ZrO_2 as a substitute for SnO_2 in white enamels is known but the former is more expensive and has less covering power than tin so attempts have been made to use the natural or normal silicate of Zr. This proves to have much less value than the pure oxide as an opacifier, but the extraction of part of the SiO_2 from the pure silicate gives a bulky product superior to ZrO_2 or SnO_2 at less cost than either."[18]

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16. Rundschau Vol.19 118-31, Chem. Abs. V (1911) 1981.
17. Grunwald Sprechsaal 44:72 Chem. Abs. V (1911) 3163.
18. Ceramique Vol.14 - 204.

Staley states that "For a given opacity it is necessary to use slightly larger amounts of zirconium oxide than of tin oxide. The enamels produced are of a slightly yellow tint and a little more refractory than tin oxide enamels made from the same formula. Up to the present time the high cost of zirconium oxide has precluded its extensive use."[19]

The treatment of zirconium silicate for the production of an opacifier has become of importance. The natural silicate does not act as a strong opacifying agent, probably because it is impossible to grind it fine enough. However, when the silicate is fused with sodium compounds a finely divided white powder is formed, which makes a very satisfactory opacifying agent.[20]

Spinel. "The spinels are insoluble aluminates. The use of these as opacifiers is an old idea, but it is only recently that they have been seriously considered.[21] Zinc spinel ($ZnOAl_2O_3$) and magnesium spinel ($MgOAl_2O_3$) are the most promising. When artificial spinels of these compositions are calcined at extremely high temperatures so as to be practically insoluble in molten enamels they make satisfactory opacifying agents. Most of the spinels put on the market so far have not been rendered sufficiently insoluble and therefore have partially dissolved in the enamel. This has reduced their opacifying power and at the same time raised the fusion point of the enamels quite materially. They produce pure white enamels of high gloss and are both cheap and non-poisonous. The use of spinels as opacifiers has many desirable features but at present must be

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19. Technologic Paper No.142 Bureau of Standards, p 57.
20. Use developed by Landau, Kreidl, Heller and Co., French patents Nos.429665, 450288, and 463623.
    Technologic Paper 142 Bureau of Standards, p 57.
21. M. Mayer and D. Havas, U.S. patent No.1104286, 1914.

considered to be in the experimental stage.[22]

B. Execution of the Work

(1) Field Covered

Three separate fields were selected for investigation of the following opacifiers:-

(1) Tin (used for comparison)

(2) Zirconia

(3) Spinel.

Limits of from 4-12% of opacifier were chosen, giving a wide margin over commercial practice, which varies from 6-10% of opacifier. The cover coat composition was selected as representative of several commercial formulae. The variations in the amounts of opacifier used in the various mixes were as follows:-

Composition No.	A_2	A_4	A_6	A_8	A_{10}	A_{12}
% Opacifier	2	4	6	8	10	12

A Series - Tin

B Series - Zirconia

C Series - Spinel.

First Batch Weight

Feldspar	194
Borax	124
Flint	80
Cryolite	50
Saltpeter	30
Fluorspar	29

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22. Technologic Paper 142 Bureau of Standards p 58. H.F.Staley.

Ceramic Formula

$$\left.\begin{matrix} .298\ K_2O \\ .454\ Na_2O \\ .248\ CaO \end{matrix}\right\} \left\{\begin{matrix} .305\ Al_2O_3 \\ .431\ B_2O_3 \end{matrix}\right\} \left\{\begin{matrix} 2.280\ SiO_2 \\ .565\ F_2 \end{matrix}\right.$$

To 100 parts of fritt add the following mill charges

Mill Charges in Parts per 100 Parts of Fritt

Material	A_2	A_{12}	B_2	B_{12}	C_2	C_{12}
Tenn. Ball Clay 7	6	6	6	6	6	6
SnO_2	4	12				
ZrO_2			4	12		
Spinel					4	12
$MgCO_3$	.9	.9	.9	.9	.9	.9

(2) Preparation of Enamels

The end members of the three series had the same fritt composition, consequently but one batch was fritted and the resulting fritt batch was divided and the six end members were weighed out and milled. The general procedure in the preparation of the cover coats was similar to that of the ground coat enamels. The water factor found to be the most satisfactory was 1.85.

Standard grades of zirconia and tin oxide were purchased from reputable concerns, while the spinel was prepared. The spinel of the $MgO\ Al_2O_3$ type was used. The two oxides were mixed in the correct molecular proportions and ground wet in a porcelain ball mill for one hour merely to insure a thorough mixture. This mixture was screened through an 80-mesh and dried to such a consistency, so as to permit it to be formed into balls. These balls were placed in alumina washed saggors and calcined in a small gas fired furnace to a temperature of 1480°C. and held for two hours.

Gas Fired Kiln

The resulting product from the calcination was submitted to a microscopist to determine the amounts of spinel formed. The results show that practically all of product was spinel, thus proving that spinel can be produced under the above condition, which is quite contrary to the assertions made by Andrew Malinovsky[23] who states that a complete liquid fusion is imperative to the formation of spinel.

(3) Trial Pieces

Steel trial pieces were produced as described on page . After pickling the steel was dipped with ground coat No.11, dried in a steam dryer and burned at 900°C. in a gas fired muffle oven.

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23. The Commercial Synthesis of Sillmanite. Chemical and Metallurgical Engineering, p 851.

(4) Application and Burning

The cover coats were applied by hand dipping, the attempt being made to obtain on all the trial pieces a coating of uniform thickness by using enamels of approximately the same water content and by allowing all the superfluous enamel to drain off. The cover coats were applied rather thinly and in two dippings, thus making two separate firings necessary. After the first dipping the enamels were dried in a steam heated dryer. Upon cooling each trial was redipped and reburned at 850°C. It was necessary to follow this procedure, in order to produce coats of sufficient thickness without peeling and crawling during burning. Three trial pieces of each composition were burned.

(5) Tests

There were three tests used in the determination of the best substitute for tin oxide.

(1) Color and Texture

(2) Reflection Test

(3) Weathering Test.

Again, the qualities, color and texture were judged by the unaided eye. The reflection test was carried on with the aid of smoke charts.* These charts are based on the theory that a perfectly black surface reflects 2% of the light that strikes it, while a white surface reflects 80%. By cross-hatching a certain percentage of the surface of the card various intermediate percentages are obtained. The trials were held against these screens and the degree of reflection was estimated. Each trial was compared with the smoke screens twice by each of the writers and an average of the four readings was made. A surprising degree of proficiency is attained with a

* Loaned by Professor Morgan Brooks, E.E. Dept., Univ. of Illinois

reasonable amount of practice.

The weathering test consisted of exposing the trials to the fumes of hydrochloric acid, sp. gr. 1.19, for forty hours. The trials were wiped and a reflection test was again applied and the difference in reflection was noted.

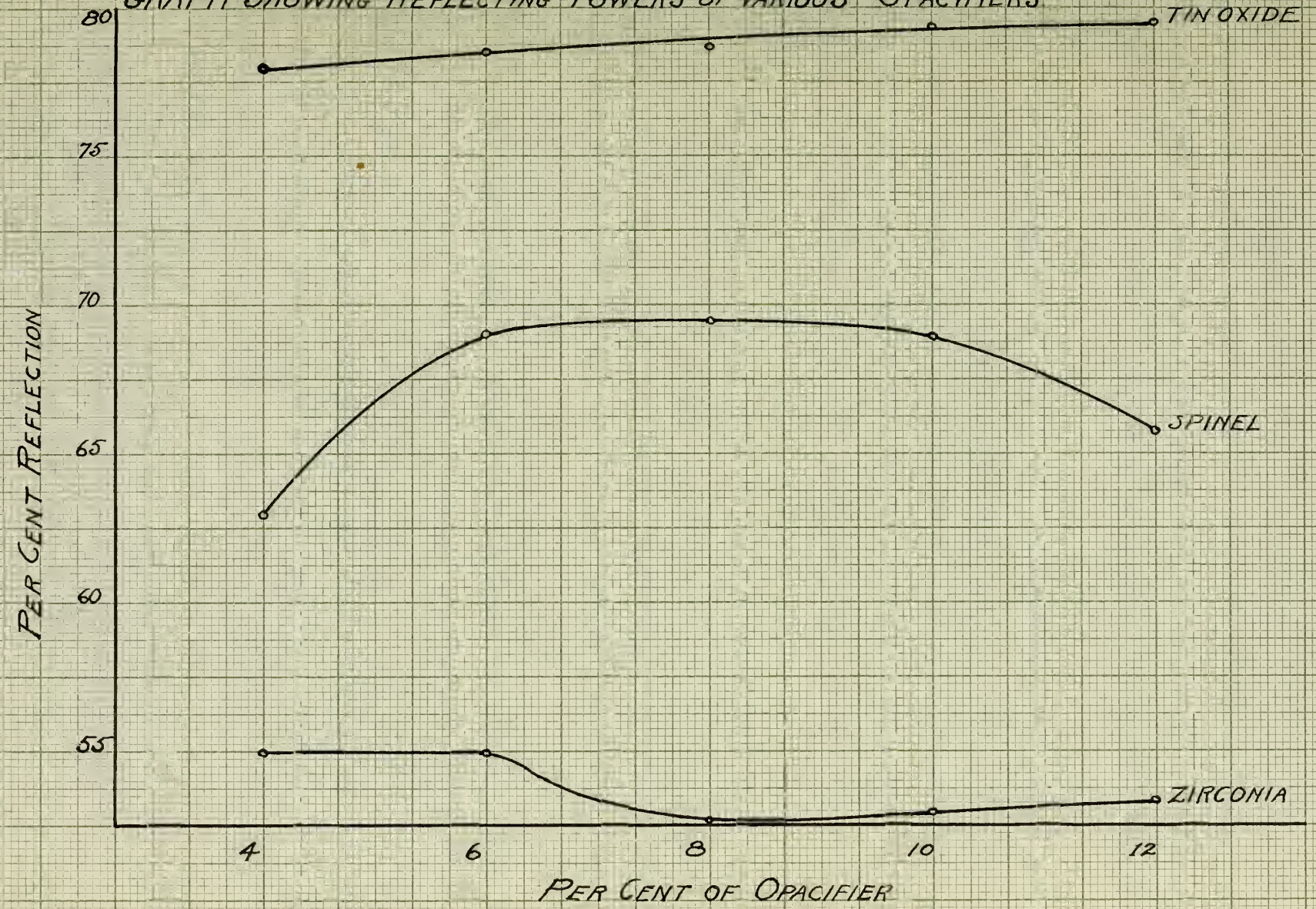
C. Results

Table of Results Showing Variation in Reflection Given by Several Opacifiers

No.	Trial	A	B	C
4	1	77%	55%	58%
	2	78	55	65
	3	78	55	35
	4	79	55	65
	Avg.	78	55	63
6	1	78	55	68
	2	79	55	69
	3	79	55	70
	4	78	55	69
	Avg.	78.5	55	69
8	1	79	52	68
	2	78	53	70
	3	78	53	68
	4	80	52	72
	Avg.	78.8	52.5	69.5
10	1	80	52	70
	2	80	52	70
	3	79	53	68
	4	78	55	68
	Avg.	79.3	53	69
12	1	80	52	65
	2	80	53	65
	3	80	53	65
	4	78	55	38
	Avg.	79.5	53.3	65.8

No. III

GRAPH SHOWING REFLECTING POWERS OF VARIOUS OPACIFIERS



D. Summary of Results

I. Color and Texture.

(a) Tin Oxide. An excellent white color and high gloss were developed on all of the trials. Both of these qualities and the covering power of the enamel was improved as the amount of opacifier was increased from 4-12%. The texture of all the trials was satisfactory.

(b) Zirconia. A highly unsatisfactory muddy grey color was obtained which gave the lowest percentage of reflection of the three opacifiers. Although added increments of the opacifying agent improved the covering power of the enamel, they did not improve the reflection. The texture was fairly satisfactory but the covering power was low.

(c) Spinel. A very good color was developed with spinel as the opacifier and a medium gloss was obtained on all the trials with the exception of A_{12}, which was rather dull probably due to the increased spinel content. The texture was entirely satisfactory.

II. Reflection Test.

(a) Tin Oxide. A slight and gradual increase in the reflecting power of the enamel was noted as the amounts of opacifier increased from 4-12%. The practical limit for the opacifier was 10%, however, a very slight increase in the reflecting power was gained with 12% tin oxide. The slight increase was not sufficient to offset the cost of the additional opacifier. The range of reflection was from 78% to 79.5%.

(b) Zirconia. Very erratic results were obtained from the reflection tests of the zirconia trials and no logical deductions could be made. A low degree of reflection (55% maximum) was obtained

(c) Spinel. A decided increase in reflecting power was noted, as the amount of opacifier increased 4-5%. Additions beyond this point slightly increased the reflecting power until a maximum of 69.5% reflection was reached at 8% opacifier. Amounts above 8% cause decreased reflection, probably due to increased refractoriness of the enamel. The covering power compared favorably with that of the tin.

III. Weathering Test.

The results obtained from the weathering tests were not consistent enough to enable the writers to deduce any well founded conclusions.

E. Conclusions

1. The practical limit for tin oxide giving satisfactory results was 10%.

2. Zirconia is not satisfactory as a substitute opacifier for tin oxide.

3. Spinel offers interesting possibilities as a substitute opacifier for tin oxide. Within the range of our investigation, the most favorable amount of the opacifier was 8%, which however was about 10% less efficient than tin oxide.

F. Comparison and Discussion of Results

In agreement with Hartman[24] and Staley[25], the writers find that zirconia decreases the covering power of the enamel as compared with tin enamels containing equal amounts of tin. The authors are of the opinion that conditions might be so regulated as to give a satisfactory gloss with the zirconia, but its poor color prohibits its usage.

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24 Rundschau Vol. 19-118.
25 Technologic Paper #142 Bureau of Standards.

The writers propose a field for further investigation, in which the boric acid and alumina contents are varied to produce a higher gloss. Another interesting possibility would be to cross the spinel with tin oxide in an attempt to reduce the amount of tin oxide necessary to produce a satisfactory enamel.

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